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Evaluation and interpretation of regional and site-specific hydrochemical data bases for water quality assessment

*M. G. Hutchins[1], B. Reynolds[2], B. Smith[1], G. N. Wiggans[1] and T. R. Lister[1]

[1] British Geological Survey, Keyworth, Nottingham, NG12 5GG.
[2] Institute of Terrestrial Ecology, Bangor Research Unit, Deiniol Rd, Bangor, Gwynedd, LL57 2UP.
* corresponding author's address: ADAS Wolverhampton, Woodthorne, Wergs Rd, Wolverhampton, WV6 8TQ. michael.hutchins@adas.co.uk

Abstract

The spatial distribution of stream water composition, as determined by the Geochemical Baseline Survey of the Environment (G-BASE) conducted by the British Geological Survey (BGS) can be successfully related under baseflow conditions to bedrock geochemistry. Further consideration of results in conjunction with site-specific monitoring data enables factors controlling both spatial and temporal variability in major element composition to be highlighted and allows the value of the survey to be enhanced. Hence, chemical data (i) from streams located on Lower Silurian (Llandovery) bedrock at 1 km^2 resolution collected as part of the G-BASE survey of Wales and the West Midlands and (ii) from catchment monitoring studies located in upland mid-Wales (conducted by Institute of Terrestrial Ecology), have been considered together as an example.

Classification of the spatial survey data set in terms of potentially controlling factors was carried out so as to illustrate the level of explanation they could give in terms of observed spatial chemical variability. It was therefore hypothesised that on a geological lithostratigraphic series of limited geochemical contrast, altitude and land-use factors provide better explanation of this variability than others such as lithology at sampling site and stream order. At an individual site, temporal variability was also found to be of considerable significance and, at a monthly time-step, is explicable in terms of factors such as antecedent conditions and seasonality. Data suggest that the degree of this variability may show some relationship with stream order and land-use. Monitoring data from the region also reveal that relationships between stream chemistry and land-use may prove to be strong not only at base flow but also in storm flow conditions.

In a wider context, predictions of the sensitivity of stream water to acidification based on classifications of soil and geology are successful on a regional scale. However, the study undertaken here has shown that use of such classification schemes on a catchment scale results in considerable uncertainty associated with prediction. Uncertainties are due to the large degree of variability in stream chemistry encountered both spatially within geological units and temporally at individual sampling sites.

Introduction

Historically, two major approaches have been adopted in hydrochemical studies of the natural environment. Surveys (e.g. Lahermo *et al.*, 1990; British Geological Survey, 1996), which involve the collection of geographically extensive data with little or no temporal resolution, seek to define regional patterns of water quality variation, thereby allowing the identification of areas at risk from pollutant contamination. On the other hand, site specific studies (e.g. Hornung *et al.*, 1985; Hughes *et al.*, 1990; Soulsby and Reynolds, 1993) involve the collection of high temporal resolution data of limited geographical extent and define controls on stream water chemical dynamics. Whilst both approaches are equally valid, a lack of interaction between scientists working in these two areas has not always allowed the interpretative value of both kinds of data to be maximised.

The objectives of this study are:

(i) to isolate specific factors influencing stream water chemical composition and quantify the influence they have on compositional variation in either temporal and spatial dimensions, and hence
(ii) to quantify the relative significance of spatial variability with respect to temporal variability, and thereby
(iii) to illustrate how baseline surveys of stream water chemistry may be exploited and enhanced by the consideration of site specific catchment monitoring studies, and also
(iv) to set a quantification of variability in the context of classification schemes for surface water sensitivity to acidification.

In this study, these objectives will be achieved mechanistically using data from the Geochemical Baseline Survey of the Environment (G-BASE) conducted at

British Geological Survey, Keyworth and from a variety of site monitoring studies undertaken by Institute of Terrestrial Ecology, Bangor.

The Geochemical Baseline Survey of the Environment (G-BASE) has been underway since the early 1970s and, in addition to its initial goal of providing regional geochemical data to be used in the identification of mineral resources, seeks to provide environmental baseline information on the surface environment of the United Kingdom. Surveying of Scotland, northern England and Wales is now complete and has largely focused on the analysis of stream sediments (e.g. British Geological Survey, 1996). More recent surveying has concentrated to a greater degree on stream water chemistry. Preliminary interpretation of stream water data from Wales and part of the West Midlands (Simpson *et al.*, 1996) has shown that it is possible to make robust interpretations of spatial patterns in terms of bedrock geology and geochemistry. Interpretation has also focused on the influence of secondary geomorphological, atmospheric and anthropogenic factors. G-BASE sampling has been conducted solely during the summer months, with the result that the majority of stream water samples reflect baseflow conditions. If prolonged differences in hydrological conditions (e.g. wet and dry summers) were to have persistent and significant effects on stream water chemistry then campaign boundaries should be expected in maps of individual determinands. Such boundaries are not evident (Simpson *et al.*, 1996). Hence, the G-BASE spatial survey provides a strong foundation for an assessment of the relative significance of temporal variability due to hydrological factors at individual sampling sites. Such significance will be set in the context of variability due to the primary bedrock geological controls and other secondary factors related, for example, to land use and geomorphology.

This study has focused on a subset of the G-BASE stream water survey (Simpson *et al.*, 1996) which spatially encompasses a number of monitoring sites investigated by the Institute of Terrestrial Ecology (Reynolds *et al.*, 1989; Stevens *et al.*, 1997). The majority of these monitoring sites are on second or third order streams. The data used in the study comprise those samples collected from streams overlying bedrock classified as Lower Silurian (Llandovery) (Fig. 1), the Telychian, Aeronian and Rhuddanian series being grouped together. Detailed lithological description of these chronostratigraphic units is available elsewhere (e.g. Holland, 1992). A limited level of contrast in major element chemistry is apparent from stream sediment data across the Llandovery (British Geological Survey, in prep.) suggesting that the observed lithological variation provides similarly limited contrast in bedrock geochemistry. The level of stratigraphic clustering used in this paper has typically been applied in the course of existing interpretation in terms of bedrock effects, both in the case of the G-BASE survey and in the course of assigning acid sensitivity classes of stream waters (Hornung *et al.*, 1990). Prediction of the sensitivity of surface waters to acidification based solely on bedrock stratigraphic subdivision (e.g. Kinniburgh and Edmunds, 1986; Hornung *et al.*, 1990) suggest that Llandovery strata provide low buffering capacity, although older Palaeozoic and Precambrian regions are predicted to give rise to even more sensitive waters.

It was intended that selection of the Llandovery subset would allow primary bedrock geochemical factors to be held constant, thereby permitting assessment of variability due to small-scale lithological and secondary (hydrological, geomorphological, anthropogenic) factors. The influence of soils is widely acknowledged in classifications of surface water acid sensitivity (Catt, 1985; Hornung *et al.*, 1990). Soil classification has not been explicitly considered in the study presented here. To summarise, much of the higher altitude eastern portion of the Llandovery is overlain by acidic soils whereas a smaller coastal region to the west is characterised by weakly or non-acidic soil cover.

Site descriptions and methods

GEOCHEMICAL BASELINE SURVEY OF THE ENVIRONMENT

The survey encompassing Wales, the Welsh borders and part of the West Midlands involved sampling of 13,345 stream waters at a resolution of approximately 1 km^2 was conducted between 1989 and 1994 during the summer months. Procedures for the sampling and analysis of stream water are described in detail by Simpson *et al.* (1993) and full details of the background rationale are given by Hutchins *et al.* (in press). In this study, interpretation focuses on major element analytical determinations but information is also available for many minor and trace elements including Al, As, Ba, Cd, Co, Cu, F, Fe, Mn, Ni, P, Pb, Sr and Zn.

SITE-SPECIFIC MONITORING

The Institute of Terrestrial Ecology (ITE) hold comprehensive data from Plynlimon, an area underlain by Lower Palaeozoic mudstones, shales and grits, dating back to 1980. Water samples have been collected at fortnightly to monthly intervals from the outflows of the Afon Cyff (C16) and Afon Gwy (W4) at an altitude of 360 m in the headwaters of the River Wye, approximately 24 km from the west Wales coast. The catchments are approximately 350 ha in area, and are comprised of acid grassland and heath vegetation, although 40% of the Cyff has been agriculturally improved. Samples from C2, an unimproved grassland 4 ha sub-catchment of the Cyff, were collected at an altitude of approximately 400 m. A fuller description of the headwaters of the River Wye is given by Reynolds *et al.* (1989) and C2 is described specifically by Chapman *et al.* (1993). During the Welsh Acid Waters Survey

(WAWS) (Stevens *et al.*, 1997), 102 acid sensitive streams were sampled on a monthly basis throughout 1995 and analysed for major and minor solutes. Of these 102 streams, 34 drain geographically varied catchments (Table 1) which have more than 95% of their area on Llandovery strata.

Table 1. Summary of attributes for the 34 Welsh Acid Waters Survey catchments located on Lower Silurian geology

Attribute	Arithmetic mean	Minimum	Maximum
Area (ha)	540.8	24.2	2510.6
Conifer cover (%)	31.1	0.0	95.5
Distance to coast (km)	89.7	23.5	243.5
Gradient (°)	8.6	6.2	13.0
Altitude (m)	235.6	160.0	340.6
Improved land (%)	12.5	0.8	36.7
Podzols (%)	80.2	24.8	100.0
Gley (%)	11.2	0.0	75.2
Peat (%)	8.5	0.0	47.8

Descriptions of analytical methods are summarised elsewhere (Stevens *et al.*, 1997; Hutchins *et al.*, in press; Rawlins *et al.*, in press) and a discussion on the selection of the Gran titration method for alkalinity determinations on samples from Plynlimon is given by Reynolds *et al.* (1986). For the WAWS survey, catchment attributes were captured using digital data held on a GIS.

SUB-CATEGORISATION OF DATA SETS

Subsets of the spatial G-BASE survey data were created using the ARC/INFO GIS. Initially, a subset of 1711 sampling sites overlying the Lower Silurian was derived excluding those sites characterised by charge balance discrepancies of greater than 25%. Small scale spatial changes in stream chemistry may be large (Billett *et al.*, 1996). Therefore, in conjunction with this subdivision, G-BASE samples from a 5 × 5 km square centred on the C2 catchment at Plynlimon were selected (38 samples). The Lower Silurian subset was then subjected to five further criteria of subdivision: stream order, land cover, lithology, altitude and distance from west coast.

In common with the entire Welsh G-BASE data set, the majority of streams draining the Lower Silurian are first order (61%), with second, third and fourth order streams comprising 31%, 7% and 1% of the subset respectively. The land cover subdivision was based on the simplified 17 class system derived from the target 25 class system available in digital form from ITE, Monks Wood (Fuller *et al.*, 1994). The classification reveals six categories to be substantially represented (see Table 6). Data from two other categories, tilled land (N) and shrub heath (I) have been included, but have been omitted from subsequent statistical tests along with 23 other sites, the majority of which are unclassified. In terms of lithology, the subdivision has been based on field observation using the petrological-mineralogical code of Harrison and Sabine (1970). Of the Lower Silurian subset, five main classes are identified (see Table 6). Some 171 samples are unclassified. The coastal proximity and altitude factors have been treated both as continuous variables and as categorical variables (divisions into 10 and 9 categories respectively) during the course of this study. The parameters measured were: shortest distance to the western coastline of Wales from sampling site; altitude of sampling site above mean sea-level. Categorical analysis of both the altitude and coastal proximity variables involved the omission of those samples more than 500 metres above sea level and more than 45 km from the coast in each case respectively. For the categorical variables, comparison of the distributions in individual chemical parameters between categories was analysed pair-wise using Kruskall-Wallis non-parametric one-way Analysis of Variance (ANOVA) (see Table 6).

G-BASE sampling is typically conducted in the period mid-June to early September. Hence, for interpretative purposes the temporal data sets from C2, C16 (Cyff) and W4 (Gwy) at Plynlimon have been subdivided into two subsets accordingly. A continuous season variable has also been derived. In this case a value has been attributed to each sample which may vary between 0 (mid-winter = 1st January) and 0.5 (mid-summer = 1st July). The relationship is linear and does not discriminate between autumn and spring sampling. The Plynlimon temporal data sets have also been attributed with a discharge variable which has also been used quantitatively for interpretative purposes. The range of catchment attributes available within WAWS are shown in Table 1. As flow was not measured at the time of sampling in WAWS, pH has been used as an indicator of flow conditions and samples at the highest and lowest recorded pH values have been selected to represent respectively low and high flow conditions. It should be noted that the low flow samples collected in the summer of 1995 were at a time of drought.

MAJOR ELEMENT COMPOSITION

Identification of broad distinctions between different stream water types in terms of their chemistry have been summarised using the diagrammatic methods of Piper (1944). Additionally, Si and pH have been used for interpretative purposes. The ionic strength of surface waters in the region under study is dominated by Na, K, Ca, Mg, HCO_3, NO_3, SO_4 and Cl. Piper diagrams consist of two trilinear plots (one for cations, the other for anions) and a bilinear plot which are generated using concentrations of the major cationic and anionic species expressed in milliequivalents per litre. The trilinear plot of cations

expresses abundance of each species (calcium, magnesium and sum of sodium plus potassium) as a percentage of their sum. The same rationale applies to the trilinear plot of anions (chloride, sulphate and sum of bicarbonate plus nitrate). These may be combined to form a bilinear plot, where the axes represent Ca+Mg (as a percentage of total major cations) and Cl+SO_4 (as a percentage of total major anions). In essence, the effects of dilution are removed by plotting the data in this way, allowing comparison of molar ionic ratios between samples of widely varying TDS (total dissolved solid) content. This is particularly useful in comparing samples collected at an individual site over a range of flow conditions. Such methods have been extensively used for the interpretation of G-BASE baseline survey of Wales and part of the West Midlands (Smith *et al.*, 1998; Hutchins *et al.*, in press)

Results and discussion

Table 2 compares the major element chemistry of the entire Lower Silurian (Llandovery) with that of the much smaller 25 km^2 subset from the Plynlimon region. The statistics highlight the acidic, base-poor, low TDS nature of streams draining Plynlimon and their apparently atypical nature in the context of the entire Llandovery. However, the Piper diagram (Fig. 2a) reveals the disparate nature of waters draining the entire Llandovery subset. The range covered on the Piper diagram is not appreciably smaller than that covered by the entire G-BASE Welsh data set (Hutchins *et al.*, in press). In this light, in terms of their chemistry, Plynlimon streams do not appear anomalous and may be considered typical of high altitude streams in Mid-Wales. The diagrams illustrate the relationship between major element stream water composition and factors such as altitude and coastal proximity.

THE EFFECTS OF SPATIAL FACTORS

Continuous variables

The effect of altitude is illustrated in Table 3 and Figs. 2b and 3. Here, concentrations of major cations and anions decrease appreciably with altitude, illustrating the effect of dilution in upland regions of high annual rainfall. Hydrogen is the only ion to show an increase. Likewise, variability in the concentrations of these elements also decreases with altitude. The decrease in variability is less obvious however. Variability for the middle altitudes digresses away from the general trend. Sodium and chloride are particularly variable for these altitude ranges. This may be due to the differing spatial distributions of the subclasses. Samples from close to sea-level were all collected at sites close to the coast. Likewise the upland samples were all located from a narrow longitudinal region. In contrast, middle altitude samples are more widely spread across the entire Llandovery region.

The Piper diagram (Fig. 2b) reveals substantial mean compositional differences between lowest and highest altitude streams. Small variations in altitude yield particularly noticeable systematic difference in chemical composition between 200 and 350 m above sea level. In Mid-Wales, it is noticeable that the division between the two classes of soils proposed by Hornung *et al.* (1990) (acidic and weakly/non-acidic) is predominately found within this altitude range. Variation in composition within each altitude sub-class is large (Table 3) and indeed in almost all cases not appreciably smaller than for the entire Llandovery data set, thereby emphasising the importance of other controlling factors. Figures 3a and 3b illustrate the compositional trends and their changing variability graphically. At higher altitudes, variability in %Ca is smaller and in %SO_4 is greater than at low altitudes. The 25 km^2 subset of Plynlimon streams, despite showing markedly less variability in composition, are typical of all Llandovery streams at high altitude.

Table 4 and Figs. 2c and 4 illustrate the subdivision of the Llandovery based on proximity to the coast. The concentration of chloride shows the most appreciable decrease in composition with distance from the coast. There appears to be some auto-correlation here with the effects of altitude. With the exception of H^+, solute content reaches a minima 25 km from the coast, where most of the highest altitude sampling locations are found. In general, variability in solute concentration is greater further inland than close to the coast. In terms of chemical composition, there is greater variability in the mean level from each class for anions than for cations (Piper diagram Fig. 2c). Increasing chloride dominance with proximity to the coast is to the detriment of sulphate. As was the case with the altitude classes, variability in composition is uniformly large within each subset, highlighting the importance of other factors. The 25 km^2 region at Plynlimon contains streams of lower TDS and higher %Na+K and %Cl than the average composition from the comparable coastal proximity sub-class.

Despite the high levels of variability observed within the altitude and coastal proximity sub-classes, multiple regression suggests that concentrations of each major species can be related with 99% confidence to these two factors alone (Table 5). Partial correlations suggest, not surprisingly, that altitude is much the more reliable predictor of major element concentration, particularly in the case of the cations.

Categorical variables

Results from analysis of subdivisions of the Llandovery based on categorical variable classes are presented for lithological, stream order and land cover subdivisions respectively. For all these classes, box and whisker diagrams are shown on Figs. 5, 6, 7 and 8 for major cations, major anions, Si, cation composition, pH and anion composition respectively. The box represents the inter-quartile

Table 2. Comparison of summary stream water chemistry data in mgl^{-1} (mean in bold, standard deviation beneath) considering: (i) entire Lower Silurian subset of G-BASE data, (ii) G-BASE data from a 25 km^2 region at Plynlimon, (iii) subdivisions of the Lower Silurian subset based on stream order, (iv) site monitoring data from streams draining 3 catchments at Plynlimon (C2, C16, W4) (with, for each site, data from the entire year in first column and data from between June and September only in the second column)

	(i)	(ii)	(iii)				(iv)					
	Total	25 km^2	1st	2nd	3rd	4th	C2	(1st)	C16	(3rd)	W4	(3rd)
number	1711	38	1047	520	128	9	256	88	578	183	545	175
HCO_3	**17.8**	**2.37**	**18.5**	**17.6**	**14.1**	**12.2**	—	—	—	—	—	—
	28.7	1.95	28.6	31.5	15.2	19.6						
Cl	**13.0**	**8.78**	**13.4**	**12.4**	**12.1**	**10.5**	**5.93**	**5.69**	**5.20**	**5.40**	**5.57**	**5.16**
	10.4	2.23	11.7	7.50	9.90	2.02	1.34	1.18	1.64	1.19	1.24	1.07
NO_3	**3.40**	**0.60**	**3.61**	**3.23**	**2.56**	**2.25**	**0.59**	**0.16**	**0.61**	**0.27**	**0.66**	**0.24**
	5.87	0.73	6.37	5.14	4.19	3.34	0.65	0.24	0.57	0.28	0.59	0.29
SO_4	**8.59**	**5.33**	**8.66**	**8.55**	**7.97**	**8.79**	**4.26**	**4.55**	**5.79**	**5.47**	**3.64**	**3.79**
	6.96	1.30	6.62	8.09	4.40	4.26	1.63	1.75	1.37	1.83	1.22	1.49
Na	**7.76**	**4.93**	**7.98**	**7.42**	**7.36**	**6.73**	**3.61**	**3.61**	**3.50**	**3.42**	**3.32**	**3.20**
	6.29	0.99	7.26	3.86	6.00	1.62	0.54	0.52	0.55	0.56	0.52	0.48
K	**1.18**	**0.13**	**1.20**	**1.22**	**0.88**	**0.70**	**0.10**	**0.04**	**0.12**	**0.08**	**0.09**	**0.06**
	3.35	0.10	3.47	3.41	2.02	0.84	0.09	0.04	0.09	0.07	0.08	0.05
Ca	**6.62**	**1.59**	**6.88**	**6.42**	**5.44**	**4.79**	**1.14**	**1.25**	**1.87**	**2.23**	**0.86**	**0.96**
	7.81	0.49	7.96	8.16	4.66	4.83	0.26	0.28	0.56	0.64	0.21	0.24
Mg	**2.61**	**0.96**	**2.66**	**2.60**	**2.27**	**2.15**	**0.73**	**0.75**	**0.99**	**1.05**	**0.69**	**0.69**
	2.85	0.22	2.77	3.23	1.59	1.65	0.14	0.13	0.18	0.20	0.12	0.12
Si	**1.95**	**1.10**	**1.99**	**1.92**	**1.74**	**1.76**	**0.92**	**0.63**	**1.12**	**1.05**	**1.09**	**1.08**
	0.93	0.36	0.96	0.90	0.76	0.44	0.34	0.19	0.26	0.27	0.27	0.27
pH	**6.67**	**5.68**	**6.67**	**6.65**	**6.70**	**6.68**	**5.50**	**5.80**	**6.22**	**6.50**	**5.50**	**5.86**
	0.78	0.58	0.79	0.76	0.70	0.77	0.42	0.30	0.48	0.39	0.55	0.49
% Ca	**31.0**	**20.8**	**31.4**	**30.3**	**30.3**	**27.9**	**20.4**	**22.0**	**27.9**	**31.4**	**17.4**	**19.3**
	10.9	4.12	11.2	10.4	9.50	9.92	2.72	2.58	4.64	3.96	2.88	2.76
% Mg	**23.3**	**21.0**	**23.4**	**23.2**	**23.2**	**23.0**	**21.8**	**21.7**	**24.7**	**25.0**	**23.1**	**23.3**
	4.08	2.21	4.40	3.58	3.25	3.11	1.80	1.91	2.03	2.20	2.33	2.42
% Na+K	**45.7**	**58.1**	**45.1**	**46.4**	**46.5**	**49.1**	**57.8**	**56.2**	**47.4**	**43.6**	**59.5**	**57.4**
	11.4	5.50	11.5	11.2	11.0	12.0	3.57	3.22	5.12	3.69	3.95	3.26
% SO_4	**23.2**	**27.3**	**22.8**	**23.8**	**23.5**	**27.2**	—	—	—	—	—	—
	7.91	3.97	8.16	7.90	5.45	6.46						
% Cl	**47.4**	**60.7**	**47.1**	**47.8**	**47.9**	**48.7**						
	13.7	5.75	13.9	13.4	13.3	14.4						
% HCO_3	**29.4**	**12.0**	**30.1**	**28.4**	**28.6**	**24.1**	—	—	—	—	—	—
$+NO_3$	17.3	6.41	17.6	17.2	15.6	18.3						

range. The lower whisker represents the maximum of 'lower quartile minus 1.5 × interquartile range' and 'minimum observation', whereas the upper whisker represents the minimum of 'upper quartile plus 1.5 × interquartile range' and 'maximum observation'. Three matrices defining significant similarities and differences between all possible paired combinations of subsets are displayed in Table 6. A key explaining the parameters represented by the matrix cells is also given in the table.

In terms of lithology, mudstones (which dominate the Llandovery), sandstones and siltstones are strongly representative of the entire data set. Shales are of significantly

Table 3. Summary data in mgl^{-1} for subdivisions of G-BASE streams draining the Lower Silurian based on altitude

altitude (m)	Total	0 50	50 100	100 150	150 200	200 250	250 300	300 350	350 400	400 450	450 500
number	1711	52	135	218	294	255	220	216	186	98	34
HCO_3	**17.8**	**43.5**	**34.4**	**24.2**	**21.3**	**18.9**	**14.1**	**9.12**	**5.89**	**6.56**	**2.87**
(mean, s.d.)	28.7	38.9	36.9	24.1	28.2	23.5	23.9	19.7	27.1	26.2	3.61
Cl	**13.0**	**24.7**	**21.2**	**16.2**	**14.6**	**11.8**	**11.2**	**9.69**	**8.60**	**8.21**	**7.10**
	10.4	9.07	10.8	10.0	17.2	4.93	7.73	4.41	2.77	4.29	1.45
NO_3	**3.40**	**9.71**	**7.42**	**5.94**	**4.44**	**3.07**	**2.16**	**1.09**	**0.68**	**0.57**	**0.72**
	5.87	7.66	9.04	6.97	5.83	3.40	6.76	1.92	1.84	1.12	1.01
SO_4	**8.59**	**12.7**	**10.8**	**9.59**	**9.64**	**9.59**	**8.49**	**6.90**	**5.68**	**5.13**	**4.66**
	6.96	9.14	4.25	3.87	4.81	5.54	9.19	7.93	5.43	3.72	1.85
Na	**7.76**	**13.4**	**11.8**	**9.45**	**8.83**	**7.38**	**7.16**	**5.92**	**5.11**	**4.86**	**4.43**
	6.29	4.59	5.31	5.45	10.2	2.59	7.91	2.62	1.33	1.57	0.63
K	**1.18**	**3.41**	**3.60**	**2.01**	**1.44**	**0.93**	**0.58**	**0.30**	**0.19**	**0.21**	**0.12**
	3.35	3.70	6.81	4.62	3.86	1.77	1.49	0.62	0.37	0.55	0.09
Ca	**6.62**	**15.6**	**11.8**	**9.00**	**7.99**	**7.15**	**5.45**	**3.58**	**2.35**	**2.42**	**1.567**
	7.81	14.3	9.01	6.18	6.34	6.82	7.55	5.65	4.50	5.71	0.82
Mg	**2.61**	**4.73**	**4.13**	**3.20**	**3.01**	**2.70**	**2.26**	**1.85**	**1.49**	**1.37**	**0.97**
	2.85	2.15	2.62	1.84	2.03	1.78	1.88	2.52	4.59	3.03	0.21
Si	**1.95**	**2.66**	**2.56**	**2.39**	**2.25**	**2.08**	**1.78**	**1.54**	**1.29**	**1.20**	**1.43**
	0.93	0.86	0.92	0.87	0.87	0.76	0.91	0.68	0.76	0.59	0.61
pH	**6.67**	**7.20**	**7.17**	**7.06**	**6.96**	**6.88**	**6.62**	**6.30**	**5.97**	**5.96**	**5.67**
	0.78	0.53	0.56	0.51	0.57	0.61	0.71	0.76	0.70	0.74	0.79

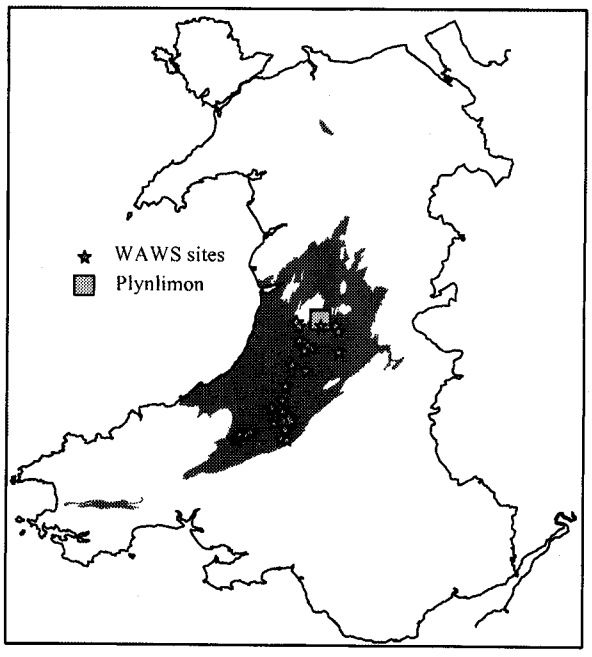


Fig. 1. *Map of Wales showing extent of the Lower Silurian (Llandovery) and location of monitoring sites.*

higher pH and, in contrast, slates significantly more acid than the mean Llandovery. Muds, silts, and sands are also generally of similar pH and % composition (anions and cations) to each other. In these respects, shales, and to a lesser extent, slates are distinct in composition, the former being of higher %Ca and $\%HCO_3 + NO_3$ and the latter of higher %Na + K and %Cl than average Llandovery. Again, variability within each sub-class (with the exception of slate) is high and is comparable to that found in the entire Llandovery.

At Plynlimon, where mudstone lithology dominates (25 km^2 subset), G-BASE stream chemistries are very much atypical of the average of all mudstones from the Llandovery. Parts of the Severn and Wye headwaters at Plynlimon are underlain by rocks of Ordovician age (Fan Shales and Fan Grits) as well as Lower Silurian (Gwestyn Shales and Frongoch Mudstones). The Ordovician strata, particularly the grits, are mineralogically much the richer in quartz and chemically poorer in magnesium, sodium and potassium oxides (Breward, 1990). Calcium oxide percentage in bulk bedrock shows little difference between Ordovician and Silurian. Locks (1996) showed that stream water composition reflected the bedrock chemistry in terms of magnesium content but not in terms of calcium

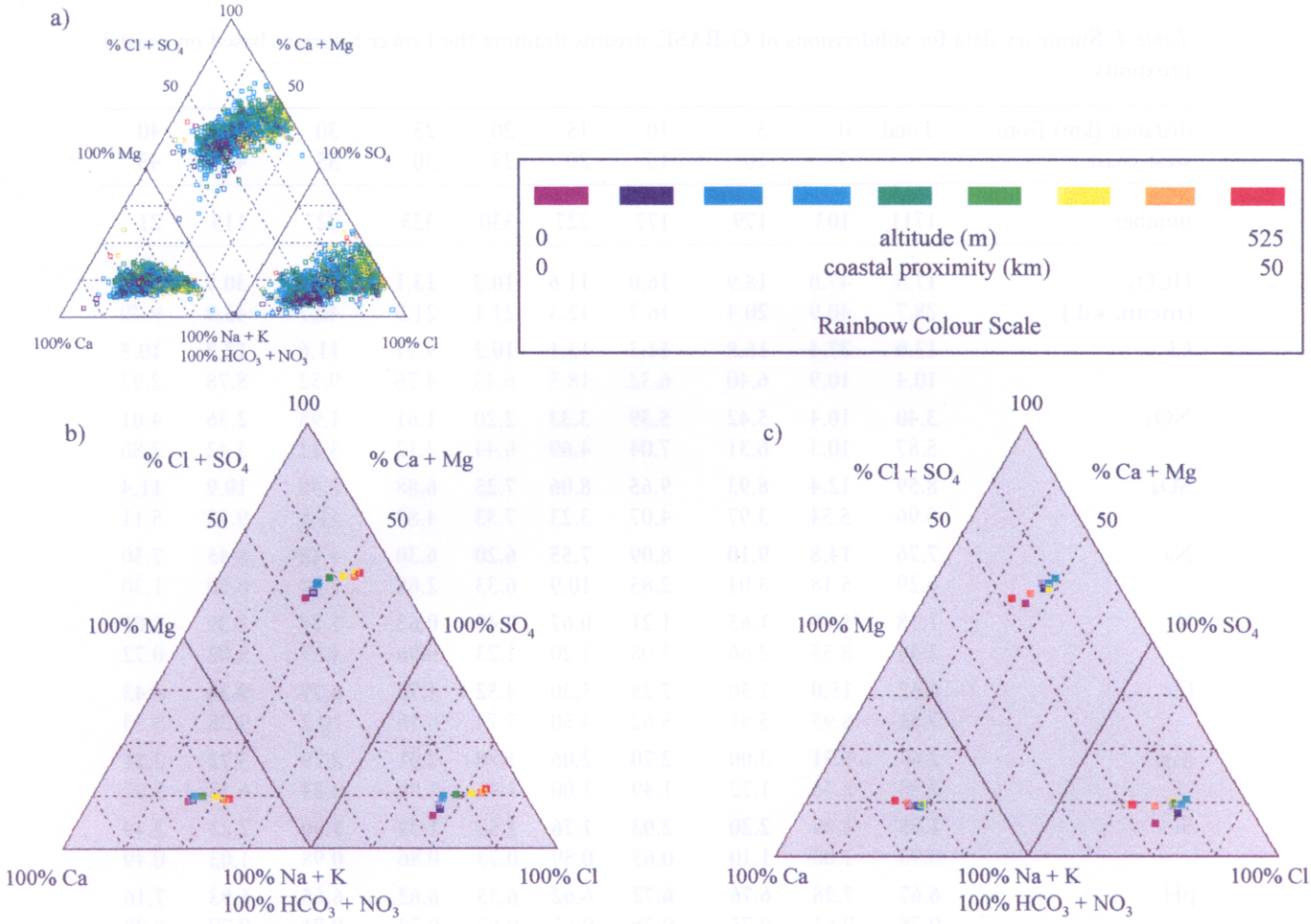


Fig. 2. *Piper diagrams depicting a subset of G-BASE data (streams draining Lower Silurian); (a) all data, discriminated by altitude, (b) mean data, discriminated by altitude for 10 class intervals, (c) mean data, discriminated by coastal proximity for 10 class intervals.*

content. In the case of both magnesium and calcium, the Silurian streams had much the higher concentrations. The occurrence or absence of mineralisation-associated calcite and its proximity to active catchment hydrological sources appears to determine predominantly stream water calcium content in this region.

Stream order appears to have little effect on the cationic and anionic dominance of Llandovery streams. Once again, variability within each sub-class is high. The matrices in Table 6 suggest little systematic difference, even in terms of single element composition, in relation to stream order.

Striking differences are apparent when the Llandovery streams are subdivided by land cover classification. Of the four predominant types (rough pasture, coniferous woodland, improved pasture and deciduous woodland) there are very few parameters revealing significant similarity in paired population tests (Table 6). Improved pasture accounts for almost 50% of the data and is most prevalent towards the south west where, to a significant regional extent, land management effects have transformed natural acidic upland soil chemistry. The differences between rough and improved pasture are very substantial, the latter generally being much higher in all solutes, particularly base cations. Consequently these streams have higher pH and %Ca and %$HCO_3 + NO_3$, the highest of all land cover types with the exception of a few samples from arable land. Compositionally, the subset from deciduous woodland falls closest to the average for the entire Llandovery and shows the highest average concentration of NO_3 and K. Coniferous woodland and rough pasture are generally similar compositionally, although the former shows uniformly higher concentrations of all solutes. When the Llandovery data set is split according to land cover, with the exception of improved pasture, variability in percentage cationic and anionic composition within the sub-classes is generally less than for any given sub-class based on the other categorical subdivisions.

CONSIDERATION OF TEMPORAL FACTORS

In this study, due to differences in the method of bicarbonate determination used between BGS and ITE projects, interpretation of results from site-specific monitoring has omitted HCO_3 and anionic composition. These

Table 4. Summary data for subdivisions of G-BASE streams draining the Lower Silurian based on coastal proximity

distance (km) from west coast	Total	0 5	5 10	10 15	15 20	20 25	25 30	30 35	35 40	40 45
number	1711	103	179	177	227	330	325	227	115	21
HCO_3	**17.8**	**47.0**	**18.9**	**16.0**	**11.6**	**10.3**	**13.1**	**20.6**	**30.9**	**24.2**
(**mean**, s.d.)	28.7	40.9	20.4	16.7	12.3	21.1	21.9	40.7	43.9	9.70
Cl	**13.0**	**27.4**	**16.8**	**14.3**	**13.1**	**10.2**	**9.77**	**11.6**	**12.2**	**10.5**
	10.4	10.9	6.40	6.32	18.5	6.43	4.76	9.52	8.78	2.93
NO_3	**3.40**	**10.4**	**5.42**	**5.39**	**3.33**	**2.20**	**1.61**	**1.98**	**2.36**	**4.01**
	5.87	10.3	6.31	7.04	4.69	6.44	2.12	3.12	3.42	3.86
SO_4	**8.59**	**12.4**	**8.93**	**9.65**	**8.06**	**7.25**	**6.88**	**8.98**	**10.9**	**11.4**
	6.96	5.54	3.97	4.07	3.23	7.33	4.82	11.8	9.15	5.11
Na	**7.76**	**14.8**	**9.10**	**8.09**	**7.55**	**6.20**	**6.30**	**7.45**	**8.45**	**7.50**
	6.29	5.18	3.04	2.85	10.9	6.33	2.68	5.84	6.50	1.30
K	**1.18**	**5.08**	**1.65**	**1.21**	**0.67**	**0.49**	**0.63**	**1.24**	**1.39**	**1.01**
	3.35	8.55	2.66	3.08	1.20	1.23	0.96	4.57	3.02	0.72
Ca	**6.62**	**15.0**	**7.50**	**7.25**	**5.30**	**4.52**	**4.78**	**6.79**	**9.36**	**8.43**
	7.81	8.95	5.91	5.62	4.50	7.74	6.18	10.2	9.38	3.53
Mg	**2.61**	**5.51**	**3.00**	**2.70**	**2.06**	**1.80**	**2.01**	**2.79**	**3.72**	**3.21**
	2.85	2.76	1.72	1.49	1.00	1.44	1.99	4.24	6.15	1.07
Si	**1.95**	**3.08**	**2.20**	**2.03**	**1.76**	**1.58**	**1.79**	**1.90**	**2.23**	**2.49**
	0.93	1.00	1.10	0.65	0.59	0.73	0.86	0.98	1.03	0.49
pH	**6.67**	**7.28**	**6.76**	**6.72**	**6.62**	**6.35**	**6.62**	**6.65**	**6.93**	**7.16**
	0.78	0.61	0.75	0.78	0.67	0.87	0.73	0.71	0.70	0.28

Plynlimon streams have been set in the context of the entire Llandovery data set and the 25 km² subset. A split has been made in Table 2 between C2 (1st order) and C16/W4 (3rd order). From the tables it is evident that even in terms of the G-BASE 25 km², the three streams are of low TDS. However, stream chemistry at C2 is thought to be influenced by calcite mineralisation (Chapman *et al.*, 1993) and this is reflected in slightly elevated pH (Table 2) and cationic composition with respect to the G-BASE 25 km². Part of the C16 catchment has undergone liming, hence calcium and magnesium content has increased and compositionally, %Ca is elevated and %Na+K decreased to levels typical of the entire Llandovery, despite the wide disparity in terms of individual solute concentrations.

Raw data show that winter seasonal maxima of K and NO_3 are apparent at all three locations (C2, C16 and W4). Loadings of sea-salts (Na and Cl) are lower during the summer months, reflecting the fact that weather systems which generate large sea-salt aerosol loadings (i.e. Atlantic depressions) are infrequent at this time of year. Temporal variability in cationic composition at these sites has also been shown in the form of trilinear diagrams (Fig. 9). These illustrate that compositional variability increases in the order C2<W4<C16. These temporally driven trends are in contrast to the entire Llandovery, within which spatial variability of 1st order streams is slightly greater than for higher order streams (Table 2). The C16 improved catchment shows considerably greater compositional variability than W4. From Table 2 and Fig. 9 it appears that this is almost entirely due to variation in calcium and to a lesser extent, magnesium. The trilinear diagrams also illustrate the degree to which variability may be explained by changes in discharge and seasonal trends. At all sites, increases in flow result in an increasing proportion of Na + K to the detriment largely of calcium. Likewise, samples collected during winter are of higher %Na+K and %Ca than during summer. For the C2 catchment, further work (Hutchins *et al.*, in press) has been carried out on compositional variability, revealing that measures of antecedent conditions can provide better explanation of variability than can be attained by purely using discharge.

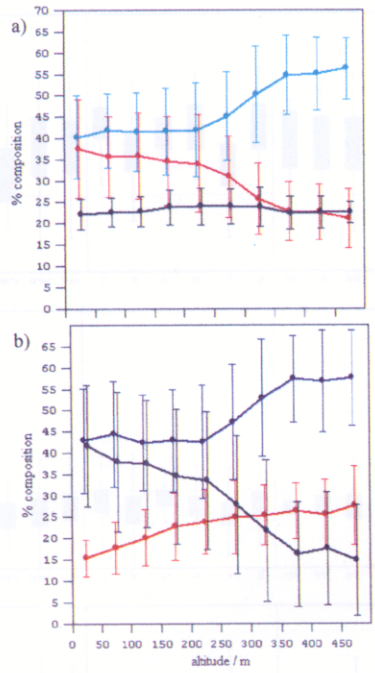
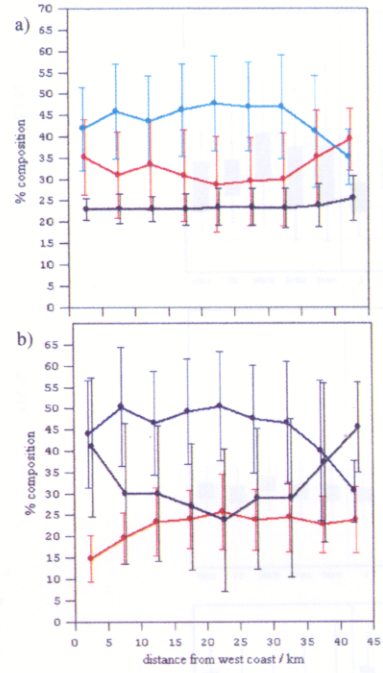


Fig. 3. *Differences in Lower Silurian streamwater composition with altitude; (a) cations, (b) anions.*



Key to Figures 3 and 4:

error bars represent
+/- 1 standard deviation

cations:

red = % Ca
cyan = % Na+K
black = % Mg

anions:

red = % SO_4
blue = % Cl
black = % HCO_3+NO_3

Fig. 4. *Differences in Lower Silurian streamwater composition with coastal proximity; (a) cations, (b) anions.*

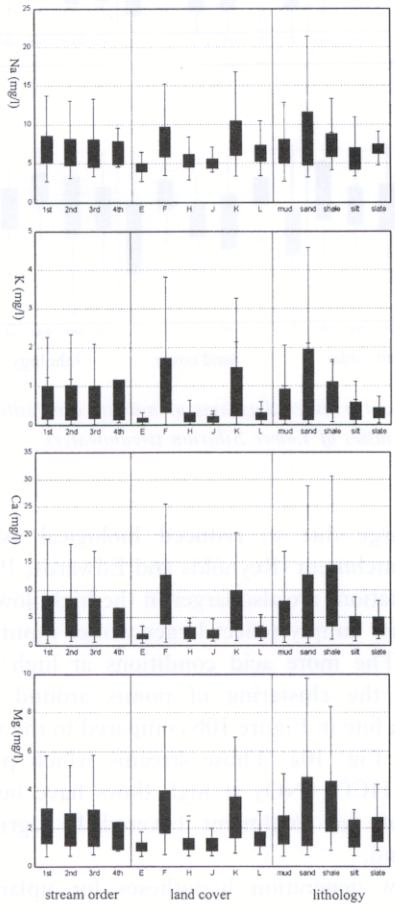


Fig. 5. *Box and whisker diagrams of cation concentration based on sub-classes of Lower Silurian streamwaters.*

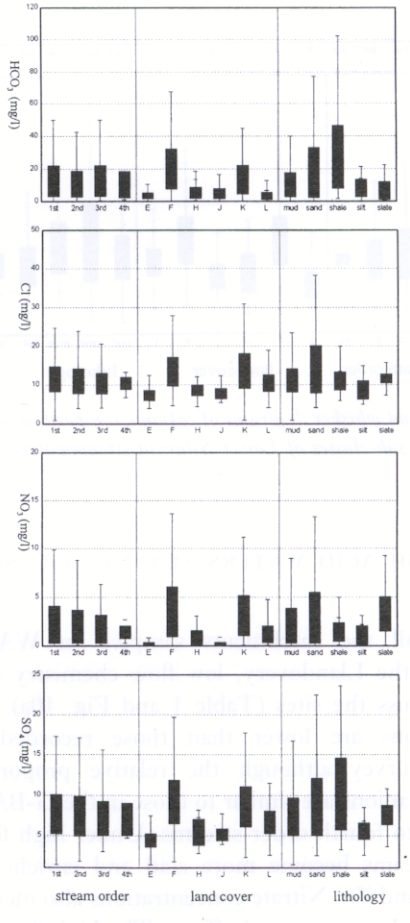


Fig. 6. *Box and whisker diagrams of anion concentration based on sub-classes of Lower Silurian streamwaters.*

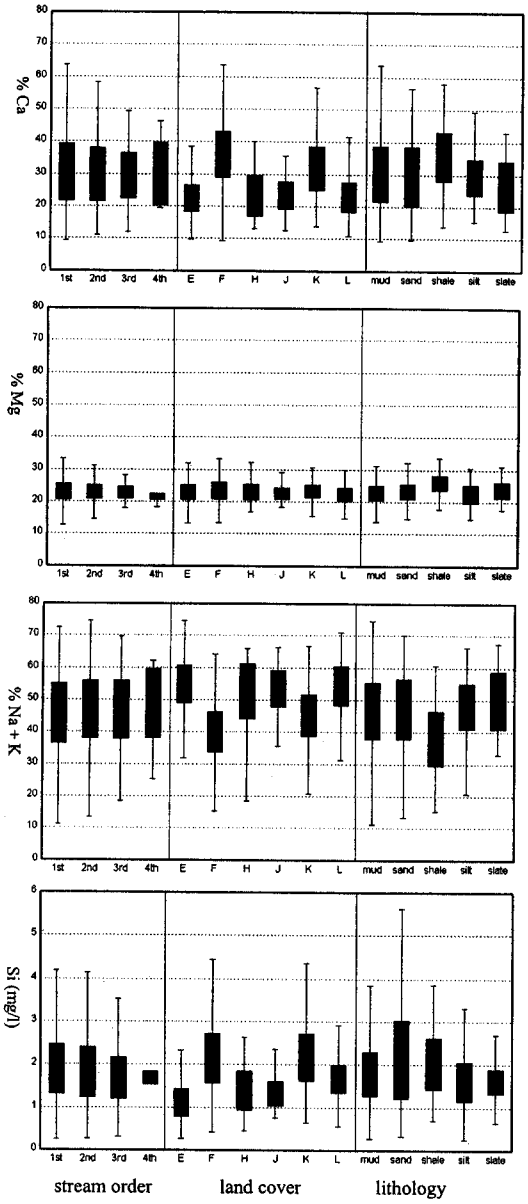


Fig. 7. *Box and whisker diagrams of cationic composition and Si content based on sub-classes of Lower Silurian streamwaters.*

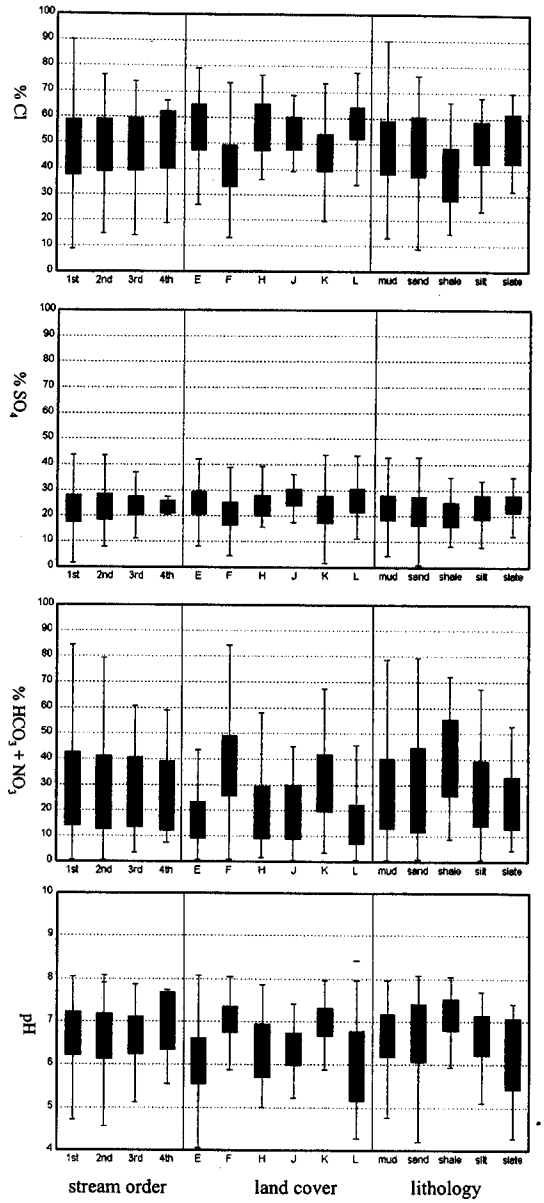


Fig. 8. *Box and whisker diagrams of anionic composition and pH based on sub-classes of Lower Silurian streamwaters.*

THE WELSH ACID WATERS SURVEY: A CASE STUDY

Although all the catchments sampled in WAWS are located on the Llandovery, low flow chemistry is highly variable across the sites (Table 1 and Fig. 10a). Average concentrations are lower than those recorded in the G-BASE survey although the relative proportions of cations and anions are similar to those in the G-BASE data for second to fourth order streams. Under high flow conditions, streams become more acid and enriched in Al, DOC, Mn and Zn. Nitrate concentrations also increase but this may be due to seasonal effects. The high flow samples were collected in the winter when soil nitrate leaching is relatively large due to reduced biological assimilation within the catchment (Reynolds and Edwards, 1995). Sea-salt concentrations are also larger in the high flow samples; again this may simply reflect larger winter inputs (Neal *et al.*, 1990). The more acid conditions at high flows are reflected in the clustering of points around the 10% HCO_3+NO_3 line in Figure 10b compared to the wider distribution in Fig. 10a. Those streams which plot on or above 30% HCO_3+NO_3 at high flows have between 20 and 30% of the catchment covered by agriculturally improved land.

Streamflow generation hypotheses for upland catchments suggest that increases in flow in response to rainfall are accompanied by an increase in the proportion of short

Table 5. Explanation of variation in chemical parameters across the Lower Silurian G-BASE subset using two continuous variables

Parameter (n = 1711) Y	partial correlation r)		ordinary least squares multiple regression (r^2)
	altitude (X_1)	distance from west coast (X_2)	$Y = aX_1 + bX_2 + c$
HCO_3	–0.313**	–0.112**	0.103**
Cl	–0.255**	–0.146**	0.158**
NO_3	–0.278**	–0.142**	0.174**
SO_4	–0.249**	0.0847**	0.0655**
Na	–0.269**	–0.0369	0.113**
K	–0.219**	–0.0322	0.0775**
Ca	–0.375**	0.0821**	0.159**
Mg	–0.273**	0.0617**	0.0845**
Si	–0.432**	0.0631**	0.221**
% Ca	–0.492**	0.232**	0.246**
% Mg	–0.0546*	0.112**	0.0125*
% Na + K	0.488**	–0.263**	0.239**
% SO_4	0.257**	0.0733**	0.121**
% Cl	0.493**	–0.362**	0.249**
% HCO_3 + NO_3	–0.502**	0.261**	0.254**

where: * = 95% confidence; ** = 99% confidence

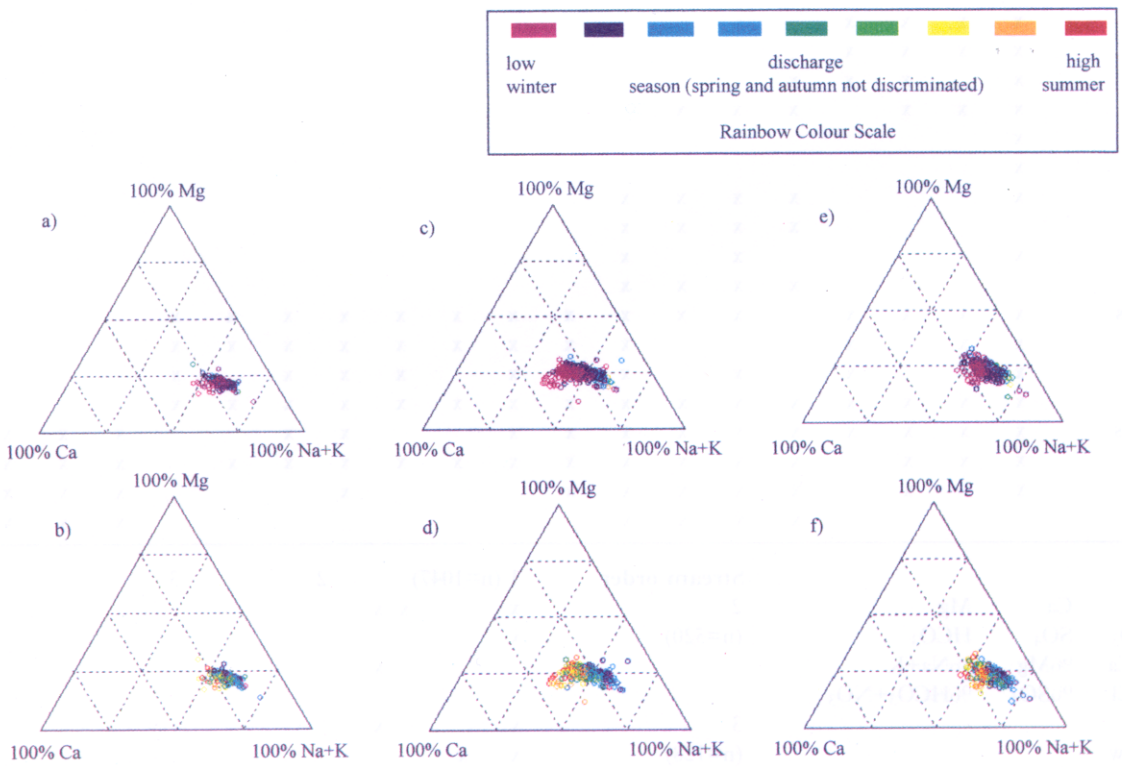


Fig. 9. *Trilinear diagrams of cationic compositional variability at Plynlimon as discriminated by; (a) discharge at C2 (1st order), (b) seasonality at C2, (c) discharge at C16 (3rd order), (d) seasonality at C16, (e) discharge at W4 (3rd order), (f) seasonality at W4.*

Table 6. **Statistical tests based on sub-categorisation of the G-BASE Lower Silurian.**

*Explanation of individual 4×4 cells in the tables (*each 4×4 cell depicts the 16 chemical parameters as in the key example above): For each possible pair of categories within a criterion (i.e. stream order, lithology or land cover type) a Kruskall-Wallis non-parametric one-way ANOVA was carried out on the 16 chemical parameters. Multiple comparisons were made using the t-distribution at 95% level. [x represents significant difference and blank a significant similarity.]*

Lithology	sandstone (n=252)				siltstone				mudstone				shale			
siltstone (n=47)	x	x		x												
	x		x													
	x															
mudstone (n=1108)	x	x		x	x											
	x		x	x	x	x	x									
	x		x													
	x		x													
shale (n=87)		x	x	x	x	x	x	x	x	x	x	x				
				x	x	x	x	x			x	x				
		x	x	x	x	x	x	x		x	x	x				
	x	x		x	x	x		x	x	x	x	x				
slate (n=43)			x		x								x	x	x	
		x		x	x		x			x		x	x		x	
										x	x		x	x	x	
	x		x									x	x	x	x	

Landcover class	Rough pasture (n = 261)				Improved pasture				Open heath				Bracken				Deciduous woodland			
Improved pasture (n=813)	x	x	x	x																
	x	x	x	x																
	x	x	x	x																
	x	x	x	x																
Open heath (n=53)	x		x	x	x															
	x	x	x		x	x	x													
	x																			
	x																			
Bracken (n=28)	x				x	x	x	x												
					x	x	x	x												
	x					x		x												
					x	x	x	x												
Deciduous woodland (n=247)	x	x	x	x		x	x	x	x	x	x	x	x	x	x	x				
	x	x		x				x	x	x	x	x	x	x	x	x				
	x	x		x		x		x	x	x		x	x	x		x				
	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x				
Coniferous woodland (n=270)	x	x	x	x	x	x	x	x	x	x			x	x			x	x	x	x
	x	x	x		x	x	x	x	x	x	x	x	x	x	x		x	x	x	x
	x		x		x	x	x	x	x				x				x	x	x	x
					x	x	x	x									x	x	x	x

Na	K	Ca	Mg
Cl	NO_3	SO_4	HCO_3
Si	%Ca	%Mg	%Na+K
pH	%Cl	$\%SO_4$	$\%HCO_3+NO_3$

* see below

Stream order	1 (n=1047)	2	3
2 (n=520)	x	x x	
	x		
		x	
3 (n=128)	x	x	
	x x		
	x		
4 (n=9)			

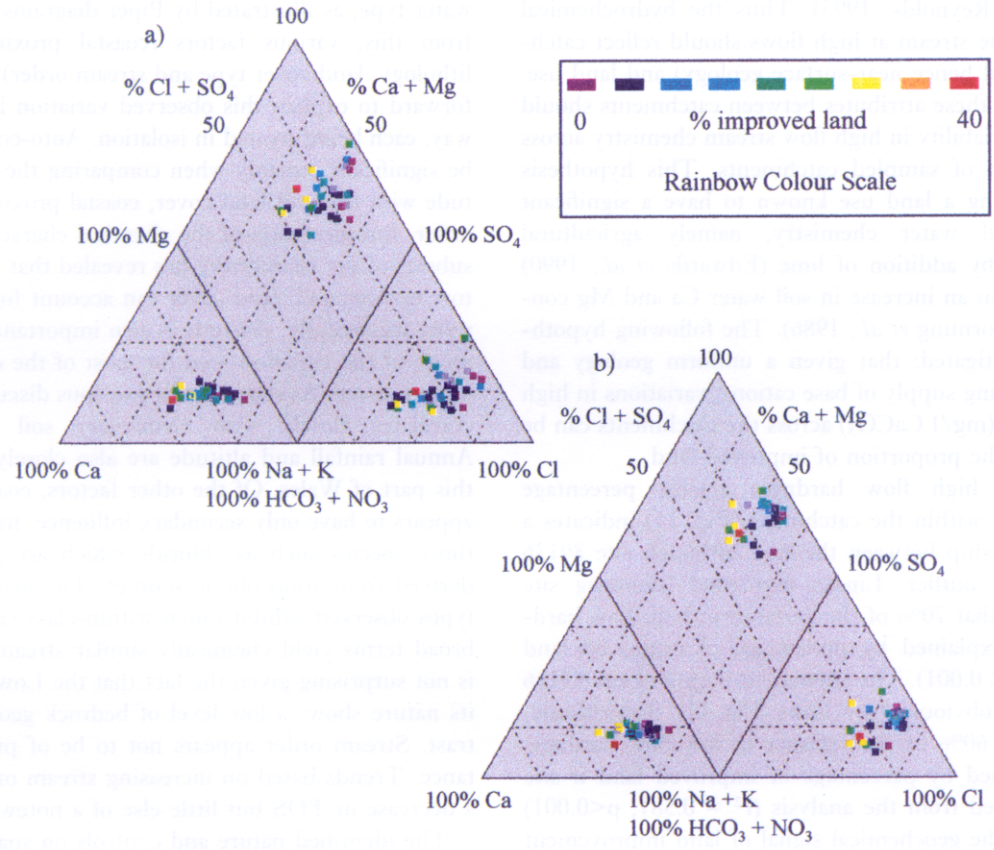


Fig. 10. *Piper diagrams depicting Welsh Acid Waters Survey catchments draining Lower Silurian (discriminated by % improved land); (a) high discharge conditions, (b) low discharge conditions.*

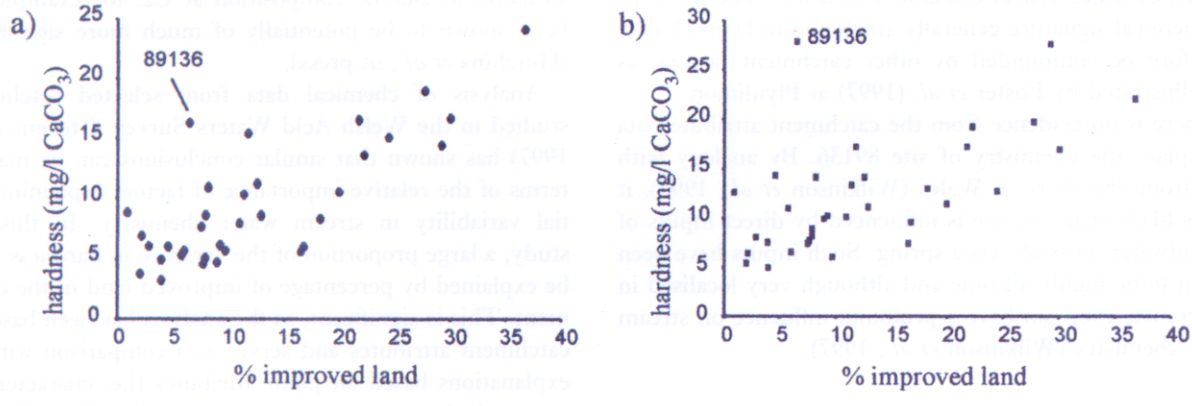


Fig. 11. *The relationship between hardness (mg/l $CaCO_3$) and percentage of improved land at Welsh Acid Waters Survey catchments draining Lower Silurian: (a) high discharge conditions, (b) low discharge conditions.*

residence-time soil waters entering the stream channel (Soulsby and Reynolds, 1993). Thus the hydrochemical signature of the stream at high flows should reflect catchment soils (and hence near-surface geology) and land use. Differences in these attributes between catchments should explain the variability in high flow stream chemistry across the population of sampled catchments. This hypothesis was tested using a land use known to have a significant effect on soil water chemistry, namely agricultural improvement by addition of lime (Edwards *et al.*, 1990) which results in an increase in soil water Ca and Mg concentrations (Hornung *et al.*, 1986). The following hypothesis was investigated: that given a uniform geology and hence weathering supply of base cations, variations in high flow hardness (mg/l $CaCO_3$) across the catchments can be explained by the proportion of improved land.

A plot of high flow hardness against percentage improved land within the catchment (Fig. 11) indicates a strong relationship between the two, although site 89136 appears as an outlier. Linear regression (omitting site 89136) shows that 70% of the variance in high flow hardness can be explained by percentage of improved land ($r^2 = 0.696$, $p < 0.001$). The anomalous nature of site 89136 becomes more obvious at low flows (Fig. 11). Surprisingly, approximately 60% of the variance in low flow hardness can be explained by percentage of improved land if site 89136 is omitted from the analysis ($r^2 = 0.581$, $p<0.001$) showing that the geochemical signal of land improvement persists even at low flows. Liming at standard agricultural rates adds a large pool of Ca and Mg carbonates to the soil which weather very rapidly compared to the alumino-silicate minerals occurring naturally within the soils or present in unweathered bedrock and this may account for the magnitude and persistence of the land use signal. The result further suggests that low flows in these catchments are sustained by long-residence time water which has drained through the soils, having acquired chemical characteristics which reflect catchment land use. The low flow geochemical signature generally attributed to bedrock may therefore be confounded by other catchment factors, as also illustrated by Foster *et al.* (1997) at Plynlimon.

There is no evidence from the catchment attribute data to explain the chemistry of site 89136. By analogy with data from elsewhere in Wales (Wilkinson *et al.*, 1997), it seems likely that this site is influenced by direct inputs of groundwater, possibly via a spring. Such inputs have been shown to be highly alkaline and although very localised in occurrence, they can have a profound influence on stream water chemistry (Wilkinson *et al.*, 1997).

Conclusions

The primary objective of the study has been to investigate the variation in major element chemistry inherent within baseline stream water sampling (G-BASE) over a single geological unit, namely the Lower Silurian (Llandovery). Emphasis has been placed on assessing the variation in water type, as illustrated by Piper diagrams. Following on from this, various factors (coastal proximity, altitude, lithology, land cover type and stream order) have been put forward to explain this observed variation in a systematic way, each being treated in isolation. Auto-correlations may be significant, notably when comparing the effects of altitude with those of land cover, coastal proximity or stream order. Interpretation of the chemical characteristics of the subsets of the Llandovery has revealed that of the five factors investigated, land cover can account for the variation most successfully. Altitude is also important in explaining much of the variation seen for most of the chemical parameters tested. As stated in the previous discussion, altitude correlates closely with elementary soil classifications. Annual rainfall and altitude are also closely correlated in this part of Wales. Of the other factors, coastal proximity appears to have only secondary influence, most notably on those species such as chloride which are predominantly derived from atmospheric sources. The major lithological types observed exhibit much within-class variation and in broad terms yield chemically similar stream waters. This is not surprising given the fact that the Lower Silurian by its nature shows a low level of bedrock geochemical contrast. Stream order appears not to be of primary importance. Trends based on increasing stream order consist of a decrease in TDS but little else of a noteworthy nature.

The identified nature and controls on spatial variability have been set in the context of temporal variations, which have been extensively characterised at three sites in the Plynlimon region. Variations may be explained by considering seasonality and hydrological conditions. The variations observed in cationic composition, for example, are of similar magnitude to the spatial variability in G-BASE samples from the 25 km^2 Plynlimon region but typically not more than 50% of that observed within the sub-classes defined from the entire Llandovery. In contrast, temporal variation in anionic composition at C2, for example, has been shown to be potentially of much more significance (Hutchins *et al.*, in press).

Analysis of chemical data from selected catchments studied in the Welsh Acid Waters Survey (Stevens *et al.*, 1997) has shown that similar conclusions can be made in terms of the relative importance of factors explaining spatial variability in stream water chemistry. In this case study, a large proportion of the variance in hardness could be explained by percentage of improved land in the catchment. This is significant, as the analysis has been based on catchment attributes and serves as a comparison with the explanations based on point attributes (i.e. characteristics at sample location) carried out using the G-BASE data. The case study has also shown that even when stormflow chemistry is used, interpretations regarding controls on spatial variability may not be greatly different from those invoked from baseflow information, hence emphasising the importance of factors such as altitude and land cover in

addition to bedrock chemistry in explaining spatial trends in regional baseline stream water survey data.

Wider implications

Given the fact that geochemical contrast is low across the lithologies observed in the Llandovery, the usefulness of multiple regressions obtained using continuous variables must be considered in a wider context. As has been demonstrated for the Llandovery, altitude and coastal proximity may be used as a basis for defining multiple regression models which predict stream water chemistry on single geological units. Factors such as land-use and lithology are likely to explain much of the scatter resultant from the existing bivariate model, which is considerable despite the high significance of the correlation coefficients. On certain other geological units the geochemical contrast is likely to prove much greater. This will focus attention more fully both on the form of such conceptual multivariate regression models and also on explanations of performance shortcomings.

At a regional scale, interpretation of stream chemistry has been successful in explaining variation in terms of bedrock geology and also of land-use and altitude. This is significant in that interpretation is consistent with existing classification schemes for surface water acid sensitivity. However, the study presented here has revealed that a great deal of compositional variation remains unaccountable. Furthermore, given the considerable temporal variation observed in individual streams and the apparent importance of surface/near-surface factors in controlling baseflow chemistry, caution is necessary if such classifications are to be extended to a smaller scale relevant to the management of water quality in individual catchments.

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